

Control of harmful hydrocarbon species in the exhaust of modern advanced GDI engines

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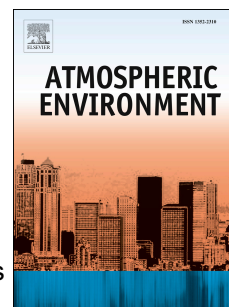
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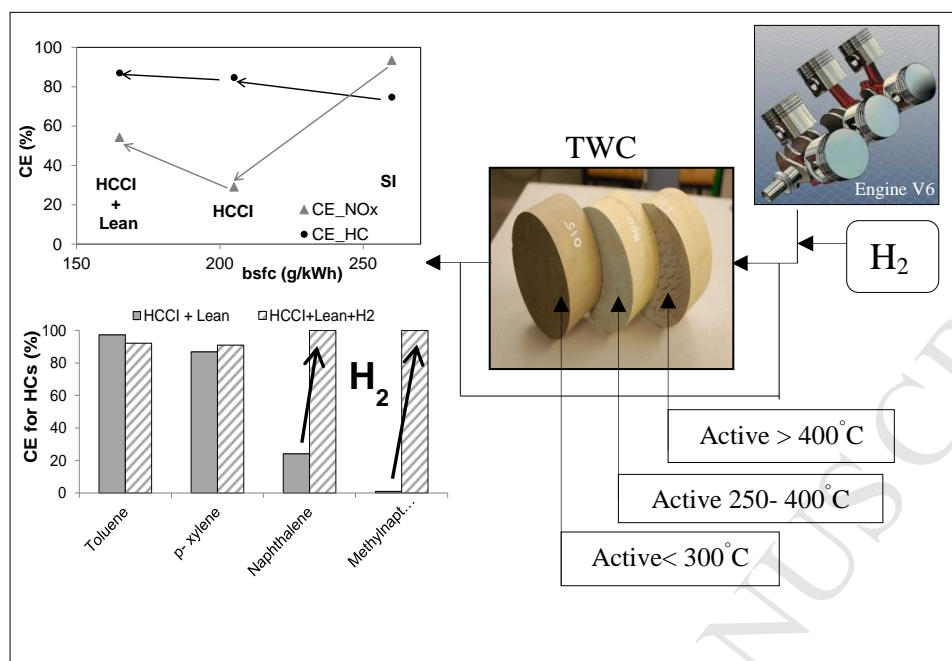
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Control of Harmful Hydrocarbon Species in the Exhaust of Modern Advanced GDI Engines

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Abstract

A qualitative and quantitative analysis of toxic but currently non-regulated hydrocarbon compounds ranging from C₅ - C₁₁, before and after a zoned three-way catalytic converter (TWC) in a modern gasoline direct injection (GDI) engine has been studied using gas chromatography-mass spectrometry (GC-MS). The GDI engine has been operated under conventional and advanced combustion modes, which result in better fuel economy and reduced levels of NO_x with respect to standard SI operation. However, these fuel-efficient conditions are more challenging for the operation of a conventional TWC, and could lead to higher level of emissions released to the environment. Lean combustion leads to the reduction in pumping losses, fuel consumption and in-cylinder emission formation rates. However, lean HCCI will lead to high levels of unburnt HCs while the presence of oxygen will lower the TWC efficiency for NO_x control.

The effect on the catalytic conversion of the hydrocarbon species of the addition of hydrogen upstream the catalyst has been also investigated. The highest hydrocarbon engine-out emissions were produced for HCCI engine operation at low engine load operation. The catalyst was able to remove most of the hydrocarbon species to low levels (below the permissible exposure limits) for standard and most of the advanced combustion modes, except for naphthalene (classified as possibly carcinogenic to humans by the International Agency for Research on Cancer) and methyl-naphthalene (which has the potential to cause lung damage). However, when hydrogen was added upstream of the catalyst, the catalyst conversion efficiency in reducing methyl-naphthalene and naphthalene was increased by approximately 21%. This results in simultaneous fuel economy and environmental benefits from the effective combination of advanced combustion and novel aftertreatment systems.

Keywords: Hydrogen, HCCI, Hydrocarbon Speciation, GDI; Three Way Catalytic Converter

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1. Introduction

The motor vehicle is a significant cause of air pollution and human health hazards, especially in urban areas. Automotive exhaust emission regulations are, therefore, becoming progressively stricter due to increasing awareness of the hazardous effects of the chemicals released by road traffic. These include environmental issues such as photochemical smog and undesirable health effects, which are caused by hydrocarbon species emitted into the atmosphere. Furthermore, it is well known that skin, lung and bladder cancer is associated with polycyclic aromatic hydrocarbons (PAHs) in the environment [1]. Therefore, in addition to the regulated engine exhaust emissions (i.e. carbon monoxide, hydrocarbons, nitrogen oxides), it is critical that unregulated species such as methane [2], carbonyl compounds [3] including aldehydes [4] and ketones [2], toluene, benzene [5] and polyaromatic compounds [6] such as naphthalene are monitored and that their impact (i.e. toxicity and photochemical reactivity) on the environment is assessed.

Gasoline direct injection engines are seen as the future of commercial internal combustion engine powertrains due to their benefits on fuel economy and gaseous emissions. However, it is reported that the levels of PM produced by these engines are higher than port fuel injection engines and diesel engines equipped with a diesel particulate filter, thus there is an increased need to investigate the emission of PM [7] and PAHs [8] by GDI engines. Due to their low emissions of NO_x and particulate matter (PM) as well as their fuel economy benefits, HCCI and lean burn engines have been also seen as enablers for cleaner vehicles. During lean combustion operation more air than needed for the combustion is induced to the cylinder in order to favour the complete oxidation, this leads to improvements in fuel economy and in-cylinder emissions formation. However, the presence of oxygen in the exhaust dramatically reduces the NO_x performance of a conventional TWC. On the other hand, in HCCI the target is to achieve low combustion temperatures and locally lean conditions in order to reduce NO_x and PM, although HCCI results in high levels of CO and unburnt total hydrocarbons emissions (THC) due to the low in-cylinder combustion temperature. Furthermore, lean HCCI leads to high levels of CO and unburnt HCs as well as the presence of oxygen in the exhaust. Due to this, there has been a growing interest over the last few years in the study of the carbonyl [9], PAHs [10] and oxygenated emissions, and their origin [11], in this type of engine running on advanced combustion operation. Most of the THCs are derived from unburned fuel being released from the crevice volumes during the expansion stroke, with increasing molecular weight of the fuel increasing the total emissions [12]. The complex reactions that take place during fuel combustion are not yet fully understood [13], but it is reported that the air/fuel (A/F) ratio plays a major role in HC emissions formation during combustion [14]. Furthermore, SI (including GDI and HCCI) engines can operate under stoichiometric, lean and rich conditions, making the function of catalysts in controlling the combustion pollutants challenging, requiring that catalytic technologies are adapted to take care of pollutants under specific conditions such as cold start and stop-start operation.

Catalysts have been used in engine exhaust aftertreatment systems for almost four decades, with continuous research and development leading to some highly effective technologies. However, there remain notable challenges associated with low temperature combustion modes such as low engine-out temperature, high unburned hydrocarbon emissions and the presence of oxygen in the exhaust in conventional TWC [15][16]. Hydrogen has been researched as an additive to improve the combustion process in GDI engines [17] and advanced HCCI combustion operation [18], as well as a low-temperature performance enhancer of different aftertreatment components such as diesel oxidation catalysts [19] and HC-SCR systems [20]. The beneficial effects of hydrogen are attributed to its exothermic oxidation increasing the temperature of the active sites as well as its chemical role as a promoter of catalytic reactions [21]. The main drawback associated with the use of hydrogen on-board a vehicle is its low density. However, it has been previously demonstrated that only small quantities of hydrogen are needed, which can be produced on-board the vehicle via catalytic fuel reforming [18][22].

In the area of hydrocarbon emissions, speciation studies are required because total elemental concentration may be uninformative and even misleading. There are no regulations or protocols established for the sampling and speciation of HC molecules. However, there are methodologies which have been adopted by international bodies for the measurement of different HC species. The Environmental Protection Agency (EPA) use the method found in [23] for the measurement of carbonyl emissions and the standard published in [24] has been used by Karavalakis et al. [25] and Fontaras et al. [26]. The Auto-Oil Air Quality Improvement Research Program (AQIRP), using capillary GC, [27], achieved separation of more than 140 compounds in the $C_1 - C_{12}$ range. This type of single-column chromatographic approach has also been used in Europe, where extensive studies have been reported [12][14]. It is become increasingly clear that speciation of the individual hydrocarbons in gasoline-engine exhaust can provide valuable information about the fuel combustion process in the engine, the performance of the emissions control systems [28] and the human and environmental hazards of the pollutants when they are released to the atmosphere.

The overall objectives of this study are to analyse different medium-to-heavy hydrocarbon species formed under HCCI and SI stoichiometric and lean engine operation, and to understand the influence of hydrogen addition on a catalyst in reducing these compounds. Hydrocarbon speciation (C_5 to C_{11}) of the exhaust gases from HCCI/SI engine operation before and after the catalyst was therefore carried out. The parameters studied here are a) engine load effect under HCCI stoichiometric condition, b) air to fuel ratio (stoichiometric and lean), c) HCCI and SI combustion modes under the same load and d) hydrogen addition upstream of the catalyst.

2. Material and Methods

Engine - The experimental engine was a 3L gasoline direct-injection (wall guided) V6 engine; the specifications are listed in Table 1. The engine was coupled to a Froude EC 38 eddy current

dynamometer. The valve-train was modified to permit operation in HCCI mode by the provision of a cam profile switching mechanism. This cam profile switching (CPS) system was used to switch between SI and HCCI modes. This system allowed on-line switching of valve lift from 9mm (SI operation) to 3mm (HCCI) operation. The HCCI operation was achieved by internal EGR, using negative valve overlap which trapped exhaust gases in order to retain enough energy for auto-ignition. The variable valve timing system of the engine made it possible to change the valve timing for the inlet and exhaust valves within a 60 crank angle (CA) degree range. More details regarding the engine can be found elsewhere in [29] and [30]. In HCCI mode the engine was operated with a wide open throttle significantly reducing pumping losses. A DSPACE- based system coupled to a computer using MATLAB/SIMULINK software was used to control the engine parameters during operation and data acquisition. The fuel flow rate to the engine was measured with the use of an AVL gravimetric meter. The fuel injection pulse width was adjusted by the engine management system to maintain the required engine operation condition and A/F ratio.

Catalyst - The 3-zone monolith catalyst (supplied by Johnson Matthey as part of the project) was connected to the actual engine exhaust manifold [31]. The first zone was designed to reduce HC and NO_x under lean and stoichiometric engine conditions at high temperatures >400°C, the second zone was designed to reduce NO_x by reaction with hydrocarbon under lean engine operation in the temperature range of 250°C – 400°C. The third catalyst zone was designed to control part of the exhaust hydrocarbons and CO at temperatures below 300°C.

Gaseous emissions analysis - A Horiba MEXA 7100 DEGR equipped with a heated line (191°C) was used to measure total hydrocarbons, carbon monoxide, carbon dioxide, NO_x and oxygen.

Fuel - Unleaded gasoline of 95 RON, composed of 48.3% saturated hydrocarbon, 16.2% olefins, 3.7% naphthenes and 30.2% aromatics, was used in this study.

Hydrogen addition - H₂ was added to the engine exhaust upstream of the catalyst and was measured using a gas chromatograph (Hewlett-Packard Model GC-5890) fitted with a thermal conductivity detector (GC-TCD).

Hydrocarbon speciation – There is no standard procedure for measuring specific HC species, as they are not individually regulated, thus both the sampling and measurement method were optimised for the experimental conditions and HC species studied. The hydrocarbon speciation of C₅ - C₁₁ was carried out using an on-line GC-MS. A Fisons 8000 series GC equipped with direct injector was connected to a Fisons MD 800 mass spectrometer, used as a detector. The gas samples were introduced via a heated line into a six-port Valco valve fitted with a 0.1ml sample loop. The gas sampling apparatus was kept at a constant temperature of 200°C. A 30m long x 0.53mm i.d. DB-1 capillary column with a 3µm film thickness was used for the separation of both the polar and non-polar compounds. The column head pressure was kept at 10psi. The helium carrier gas flow rate was

controlled at a flow rate of 6ml/min. The temperature programme settings (Table 2) were set to flush the heavier hydrocarbons from the column. As there is no established reference procedure and in order to ensure the accuracy of the results, standard mixtures of paraffins, olefins and aromatics with known concentrations were used to calibrate the chromatograph. The components of the standards sample were generally stable under the operation conditions used in this analysis. The retention time of each species was calibrated daily before each set of experiments, by the analysis of a 15 component reference gas (sourced from BOC). The total run time was 20 minutes for the retention times of the species given in Table 3. The integrated area of each specific peak in the chromatogram was used to calculate the concentration of the associated component. The VG Mass-Lab software was used to acquire and integrate the basic GC-MS data.

Hydrocarbon species – The individual compounds that are quantified in this study were chosen because of the impact they have on air quality and ultimately to human health. The Occupational Safety and Health Administration (OSHA) have introduced permissible exposure limits for these species. The limits (are time-weighted average values, calculated for an exposure time of 8 hours. The individual limits are shown in Table 4 [32]. General information regarding the studied species is given below.

Iso-octane is studied as it is a major component in gasoline fuels. Iso-pentane is chosen as one of the typical hydrocarbon species derived from iso-octane. Benzene has been chosen as it has been classified as human carcinogen by the Environmental Protection Agency (EPA). Toluene, which is a derivative of benzene, is another major component of gasoline fuels and one of the major volatile compounds in the atmosphere [33]. It has been reported that the higher the content of toluene, iso-octane and aromatic hydrocarbons in the parent fuel the higher the benzene concentration formed during combustion [15][34].

Ethyl-benzene has been classified as possible human carcinogenic by the International Agency for Research on Cancer (IARC) [35][36]. It is a major combustion by-product of aromatic species such as xylene isomers during the combustion process [37]. It also participates in the formation of benzene, toluene [38] and PAHs. P-xylene, which is also included in this study, is often formed by the replacement of two hydrogen atoms of benzene by methyl groups, during the combustion process.

Naphthalene has been studied as it has been reported to be the most abundant PAHs in polluted urban atmospheres [39]. It has been defined as a hazardous air pollutant by the US environmental protection agency (EPA) [40] and classified as possibly carcinogenic to humans by the international agency for research on cancer (IARC) [35]. Finally, methyl-naphthalene is monitored, which could be formed from two benzene rings joining together while simultaneously a hydrogen from the naphthalene group can be replaced by a methyl group [41].

Engine operation condition – Two different engine operating conditions defined by engine speed and load have been chosen. Those engine conditions selected are representative of a wide range of

urban driving conditions of the vehicle equipped with this engine, where the exhaust conditions (i.e. low temperature and high HC emissions) are challenging for efficient catalyst operation (Table 5). The influence of the combustion mode (SI or HCCI), engine load (3bar or 4bar NMEP) and A/F ratio (stoichiometric or lean) in the engine output concentration of NO_x and the magnitude and speciation profile of THC emissions has been studied.

3. Results and Discussion

3.1 Engine-out hydrocarbon species emissions

Engine output NO_x and hydrocarbon speciation comparing HCCI and SI stoichiometric combustion modes were carried out at 4 bar NMEP engine operation condition. Engine output NO_x emissions were reduced around 4x times while the total concentration of C₅-C₁₁ hydrocarbon species was approximated 12% higher under HCCI stoichiometric in comparison to stoichiometric SI engine operation (Table 5 and Figure 2). In general terms, the engine output emission concentration for all the studied species were higher for HCCI combustion with the exception of benzene, ethyl-benzene and iso-octane (Table 6 and Figure 3). The higher unburned hydrocarbon emissions under HCCI combustion are due to the lower in-cylinder temperature and available energy to drive the complete oxidation reactions of the hydrocarbons part of the fuel and to also reduce hydrocarbon oxidation post combustion. On the other hand, the lower concentration of the rest of species under HCCI conditions can be attributed to i) the conversion of iso-octane to methane [42] (this finding supports the results of a previous study from this group where high concentration of methane was found under HCCI stoichiometric engine operation [31]), ii) a higher formation rate of toluene, p-xylene, naphthalene, methyl-naphthalene or any other compounds derived from benzene due to the higher presence of hydrocarbon to react with, and iii) the breakdown of the already formed toluene and p-xylene during SI combustion process producing benzene and ethyl-benzene.

The engine operation at lean HCCI combustion enables simultaneous reduction of both NO_x and the total hydrocarbon concentration of the species from C₅ to C₁₁, compared to HCCI stoichiometric operation (Figure 2). HCCI lean operation especially reduces very harmful aromatic compounds such as p-xylene, naphthalene and methyl-naphthalene, while mainly increasing iso-pentane (alkane) and iso-octane. Total C₅-C₁₁ unburned hydrocarbon emissions were reduced when increasing the engine load under both lean ($\lambda=1.4$) and stoichiometric HCCI operation (Table 5). Under HCCI stoichiometric operation, increasing the engine load reduces the total hydrocarbon species in the range of C₅ to C₈, while increasing the naphthalene and methyl-naphthalene engine output emissions (Table 6). This phenomenon could be attributed to the higher in-cylinder temperature at high load which could increase the reaction rate of naphthalene formation through the fusion of two benzene rings. Further reaction pathways will form methyl-naphthalene, by replacing the hydrogen atoms by methyl groups [41]. A second mechanism for this could be the cyclisation of long-chain hydrocarbons found in the partial combustion products. At lean HCCI operation the engine output concentration of all the

species are reduced when engine load is increased (Table 6). It is suggested that the temperature in the post-combustion phase of the engine cycle, where naphthalene is formed [43], is not high enough to significantly enhance naphthalene formation at any of the studied loads under lean combustion operation.

3.2. Catalyst conversion efficiency

The NO_x conversion of the catalyst was significantly decreased under HCCI stoichiometric operation in comparison to stoichiometric SI (Figure 4). However, the total hydrocarbon conversion (C₅-C₁₁) at 4bar NMEP for HCCI stoichiometric operation was even higher compared to stoichiometric SI operation, despite the large reduction in the exhaust gas temperature. Figure 4 also shows that HCCI lean operation at 4bar NMEP enables an increase in both NO and HC conversion by the catalyst, when compared to HCCI stoichiometric operation.

The average conversion of HC species over the catalyst under both SI and HCCI combustion modes was higher than 90% for all engine conditions, except for HCCI stoichiometric operation at 3bar NMEP (Figure 5). Figure 5 (bottom) shows that the catalytic conversion was reduced to 60% for most of the hydrocarbon species at HCCI stoichiometric operation. It is as though, at these low exhaust gas temperatures, only the 3rd catalyst is active in oxidation of C-containing species (Table 5, Figure 1), thus under these conditions i) the effective space velocity (SV) is significantly increased as only 1/3 of the catalyst array is active, and the presence of available oxygen is required to catalytically oxidise the HC species in the catalyst active sites. Therefore, the low exhaust temperature and absence of oxygen in stoichiometric HCCI operation at low load resulted in the reduced HC oxidation rates. As expected, hydrocarbon conversion over the catalyst was significantly improved for HCCI lean operation (second zone of the catalyst is also active thanks to the higher oxygen availability) and at high engine load conditions (higher exhaust gas temperatures activating all the three catalyst layers). For instance, the conversion of iso-pentane was approximately 63% during HCCI stoichiometric operation and improved to 93% during HCCI lean operation (Figure 2), this is despite the compound being a saturated alkane (ie with single C-C bonds). Iso-octane conversion was approximately 65% during HCCI stoichiometric operation at low load, and as the temperature was increased (i.e for high load SI mode, Figure 3 condition 5) the net conversion rose to 100%.

The conversion efficiency for light aromatic HC components, i.e. benzene and toluene was high for most engine conditions. For the aromatic hydrocarbon p-xylene (a benzene ring with two methyl substituents), an average of 85% catalyst efficiency was achieved. However, for heavier and more dangerous aromatic compounds that are known to be difficult to combust catalytically [44], such as naphthalene and methyl-naphthalene, the catalyst conversion was in the range of 15-80%. The low conversion could be because the aromatic rings are more susceptible to further dehydrogenation than to combustion. As a result, the contact time required for catalytic combustion of heavy aromatic species is longer than that for saturated HCs, which reduces the probability of naphthalene and

methyl-naphthalene decomposition to smaller hydrocarbon species [44][46]. Conversion was improved at higher temperatures as the kinetic limitations to combustion were overcome [42]. Storage of some of the HC species, including both naphthalene and methyl-naphthalene, is expected to occur in the middle zone, which contributes to the reduction in the concentration of these species.

3.3 Catalyst performance with H_2 addition, HCCI lean operation

The effect of hydrogen has been investigated by injecting approximately 2400 ppm H_2 upstream of the catalyst, in order to improve the catalyst performance in the reduction of harmful HC species such as naphthalene (classified as possible carcinogenic by IARC) and methyl-naphthalene. Comparison is drawn between the same engine operating condition (lean HCCI combustion at 4bar NMEP) with and without hydrogen addition, (Figure 6 and 7).

From the results it can be observed that hydrogen greatly enhances the catalyst performance by 66% and 100% respectively (Figure 6) in reducing naphthalene and methyl-naphthalene (Figure 7). There are several likely causes: (i) Hydrogen oxidation in the first zone increases the catalyst temperature by 5 to 20°C, enhancing the oxidation rate of the aromatic hydrocarbons (ie the exothermic effect of hydrogen); (ii) We have earlier reported that hydrogen oxidation in for example a Pt/ Al_2O_3 catalysts, increases the availability of NO_2 that is consequently consumed in the oxidation of the C-containing species [19]; (iii) Hydrogenation is another possibility, in which H_2 reacts with the aromatic compounds to form less unsaturated cyclic and aliphatic hydrocarbons that are easier to combust. However, although the hydrogenation reactions are overall exothermic, there is a high activation barrier to overcome.

4. Conclusions

Engine operation under low temperature combustion and lean engine operation strategies enable the simultaneous increase in fuel efficiency and a decrease in both NO_x and particulate matter emissions. However the CO and unburnt HC emission levels increase, while the low exhaust temperature and presence of oxygen result in more challenging conditions for conventional aftertreatment devices to reduce CO and unburnt hydrocarbon emissions.

In this research a catalytic system was evaluated with the aim of oxidising the HC species produced under those fuel-efficient, but challenging exhaust conditions. Exhaust hydrocarbons have been speciated, and the efficiency with which they are oxidised by the catalyst has been assessed under different engine operation conditions. Species such as iso-octane, benzene, and ethyl-benzene are mainly found in the engine exhaust during SI engine operation, while heavier species such as naphthalene and methyl-naphthalene are present in higher concentrations under stoichiometric HCCI engine operation.

The three-zone catalyst reduced most of the hydrocarbon compounds in both (HCCI and SI) combustion modes, except for methyl-naphthalene and naphthalene, which are known to be hazardous

both to the environment and to human health, and are commonly found in the atmosphere in urban areas. The catalyst was, therefore, less capable of activating a fused pair of benzene rings than aliphatic or mono-aromatic molecules. However, the addition of hydrogen upstream of the catalyst during HCCI lean engine operation substantially enhances the conversion of both methyl-naphthalene and naphthalene species. This is attributed to an increase in the local temperature as a result of hydrogen oxidation, and due to its reactivity with the aromatic compounds to form molecules that are more readily oxidised by the catalyst. Therefore, this research work has demonstrated that, through the integration of advanced combustion technologies with novel aftertreatment systems, it should be possible to achieve notable benefits in fuel economy and in air quality.

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Abbreviations

AQIRP	Auto-Oil Air Quality Improvement Research Program
A/F	Air to fuel ratio
Al₂O₃	Alumina
BOC	British Oxygen Company
CA	Crank Angle
CO	Carbon Monoxide
CPS	Cam profile switching
EGR	Exhaust Gas Recirculation
EPA	Environmental protection agency
GC-MS	Gas chromatography-mass spectrometry
GC-TCD	Gas chromatography-thermal conductivity detector
GDI	Gasoline direct injection
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
IARC	International agency for research on cancer
NO_x	Nitrogen oxide
NO	Nitrogen Monoxide
NO₂	Nitrogen dioxide
NMEP	Net Indicated Mean Effective Pressure
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate Matter
Pt	Platinum
RON	Research Octane Number
SI	Spark Ignition
SV	Space Velocity
THC	Total Hydrocarbon
TWA	Time-weighted average
TWC	Three-way catalytic converter

List of tables

Table 1. Engine specification summary.

Table 2. GC operating parameters.

Table 3. Retention times of detected compounds.

Table 4. Permissible exposure limits [27].

Table 5. Engine conditions and emissions under HCCI and SI modes at 2000 rpm speed.

Table 6. Concentration of hydrocarbon species (C₅ – C₁₁) before and after the catalyst for the different engine conditions at 2000rpm engine speed.

Table 1

Description	Specification
Engine type	V6, 24-V, GDI
Bore	89mm
Stroke	79.5mm
Fuel	Gasoline, RON 95
Compression ratio	11.3
Intake valve timing	Variable
Exhaust valve timing	Variable
Intake temperature	Variable

Table 2

Instrument Parameters	Description
Column	DB-1; 30m; 0.53mm ID; 3 μ m film
Detector	MS; Source 200°C
Oven Temperature	40°C initial; 5 min hold, 10°C/min to 240°C; 5 min hold,
Flow Rate	6ml/minute; He

Table 3

Peak NO	Compound	Retention Time (minute)
1	iso-pentane	3.77
2	benzene	7.04
3	iso-octane	7.85
4	toluene	9.42
5	ethyl-benzene	11.54
6	p-xylene	11.72
7	naphthalene	18.19
8	methyl-naphthalene	20.66

Table 4

Chemical Species	Exposure Limits (ppm) TWA
iso-pentane	1000
Benzene	1
iso-octane	300
Toluene	200
ethyl-benzene	100
p-xylene	150
Naphthalene	10
methyl-naphthalene	N.A

TWA- time weighted average

Table 5

Engine Condition	Mode	HCCI	HCCI	HCCI	HCCI	SI	HCCI+H₂
	λ	1.0	1.0	1.4	1.4	1.0	1.4
	NMEP (bar)	3.0	4.0	3.0	4.0	4.0	4.0
	O ₂ (%)	1.2	1.2	6.29	6.55	1.06	6.55
	CO ₂ (%)	12.31	13.92	10.31	10.34	13.81	10.34
	C ₅ -C ₁₁ (ppm)	1718	1683	1731	1222	1500	1222
	T _{Ex} (°C)	385	413	349	386	661	406

Table 6

Compound	HCCI $\lambda=1, 3.0\text{bar}$ (ppm)		HCCI $\lambda=1, 4.0\text{bar}$ (ppm)		HCCI $\lambda=1.4, 3.0\text{bar}$ (ppm)		HCCI $\lambda=1.4, 4.0\text{bar}$ (ppm)		SI $\lambda=1, 4.0\text{bar}$ (ppm)		HCCI+H ₂ $\lambda=1.4, 4.0\text{bar}$ (ppm)	
	B	A	B	A	B	A	B	A	B	A	B	A
iso-pentane	150	55	100	15	174	15	125	8	36	6	125	39
benzene	72	25	58	2	68	0	52	4	140	10	52	27
iso-octane	151	52	N.A	N.A	180	39	160	27	80	0	160	N.A
toluene	597	144	420	41	616	30	508	14	345	34	508	40
ethyl-benzene	130	29	105	19	N.A	N.A	N.A	N.A	115	19	N.A	N.A
p-xylene	454	115	442	46	476	20	296	39	360	63	296	27
naphthalene	114	55	344	69	170	144	58	44	335	159	58	0
methyl-naphthalene	50	33	214	66	47	42	23	23	89	89	23	0
Total C ₅ -C ₁₁	1718	508	1683	258	1731	290	1222	159	1500	380	1222	133

B- before catalyst

A- after catalyst

List of Figures

Figure 1. Schematic of experimental setup.

Figure 2. Engine output C₅-C₁₁ hydrocarbon species and NO_x at 4bar NMEP and different combustion conditions.

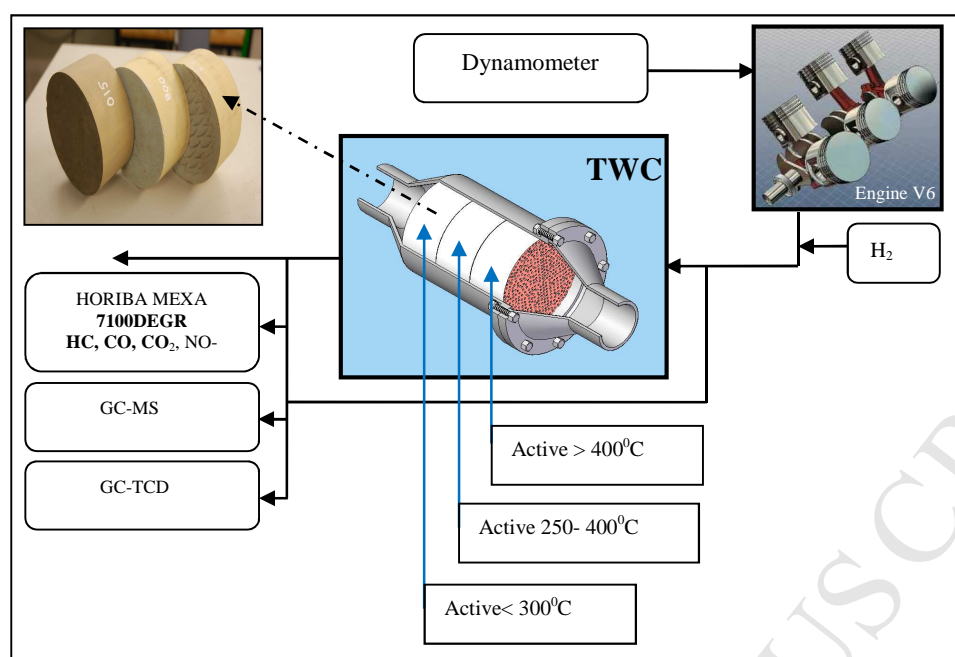
Figure 3. Engine output HC species at 4bar NMEP at different combustion conditions.

Figure 4. Conversion efficiency of the catalyst at 4bar NMEP and different combustion modes.

Figure 5. HC conversion efficiency of the catalyst at different combustion conditions 4bar NMEP (top) and 3bar NMEP (bottom).

Figure 6. HC conversion efficiency of the catalyst at 4bar NMEP with and without hydrogen addition.

Figure 7. Hydrocarbon concentration downstream of the catalyst with and without hydrogen addition.

**Figure 1**

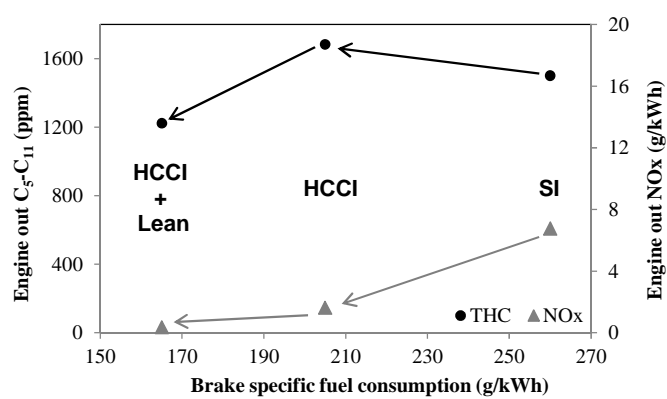
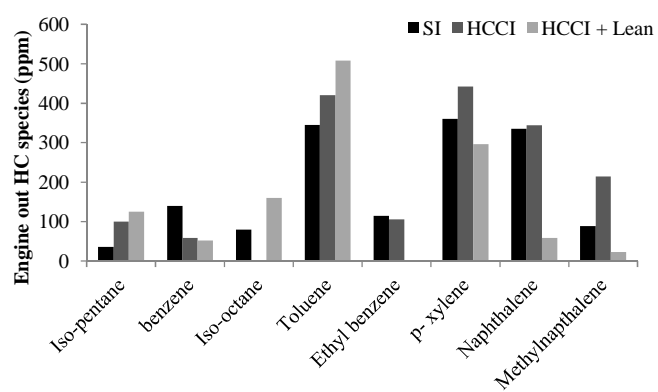


Figure 2

**Figure 3**

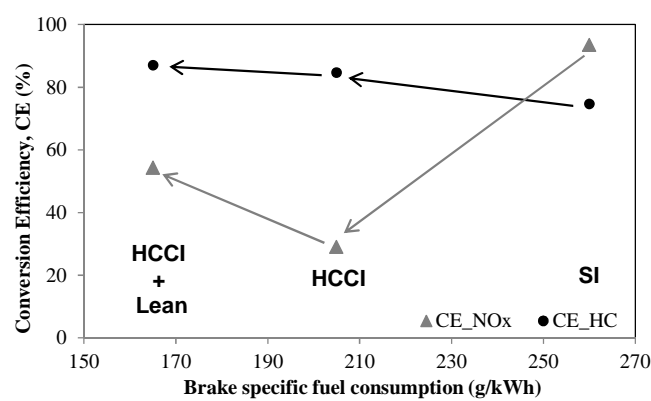


Figure 4

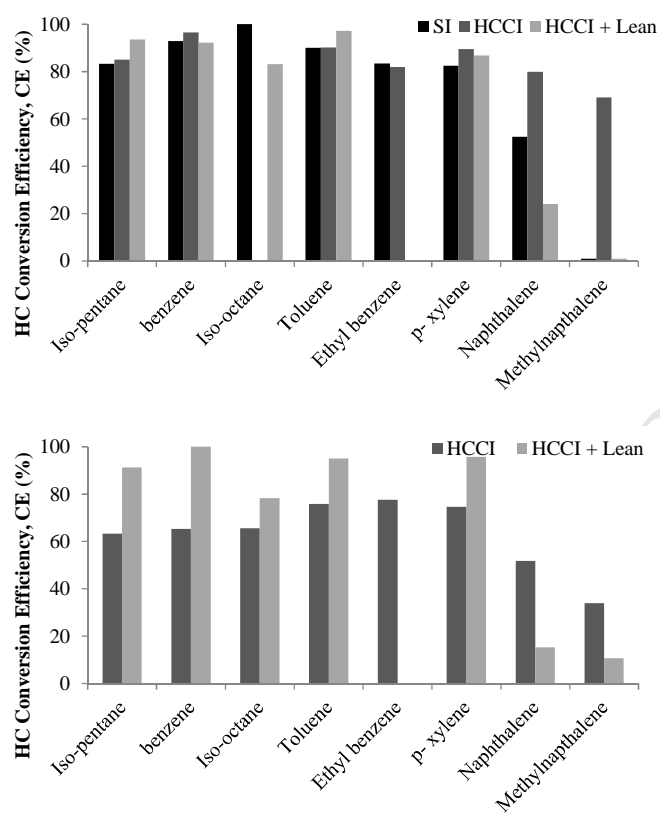
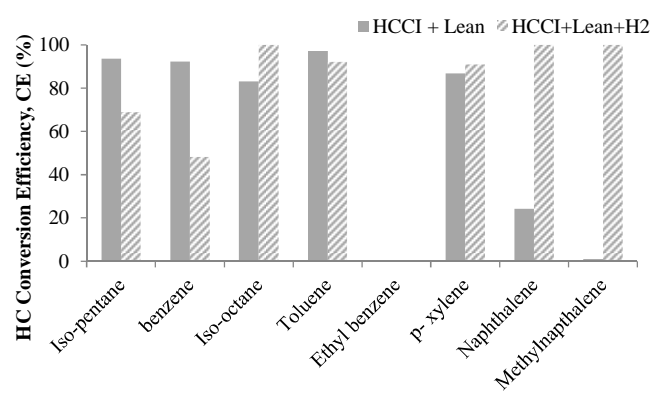
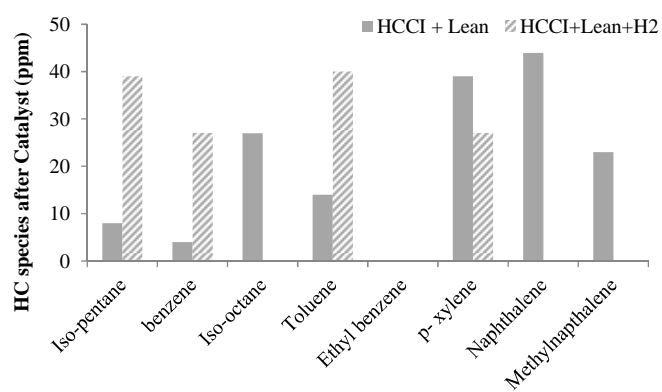


Figure 5

**Figure 6**

**Figure 7**

Toxic non-regulated hydrocarbon compounds C₅ - C₁₁ from modern GDI engine were analysed

The analysis was carried out for stoichiometric and lean combustion engines.

The catalyst ability to control heavy HC (C₅ – C₁₁) was also studied

Naphthalene and methylnaphthalene were the most resistant compounds

Hydrogen addition in the catalyst improved methylnaphthalene and naphthalene reduction